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AN ANALYTICAL STUDY OF THE CONTINUOUS CHEMICAL
REGENERATION OF SURFACES

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SUMMARY

Chemical means of preventing the destruction of hot metal surfaces by sublimation have been known for some time. The present report contains an analysis of this so-called regenerative process in which gaseous materials such as chlorine react with the sublimating metal and transport it back to the hot surface in the form of a gaseous compound. The systems were considered to consist of two solid surfaces at differing temperatures with a gas-filled interspace. The major assumptions were that the gas phase is a continuum in which local chemical equilibrium exists and that the mass transport is described by ordinary gaseous diffusion equations.

The conditions within the system required to prevent the destruction of the solid surfaces were discussed. Some of these conditions, employed in a simplified analysis, resulted in thermodynamic criteria for selecting the materials to be tested in regenerative systems.

As an illustration of some of the principles discussed, these hypothetical systems were considered: tungsten-chlorine, molybdenum-chlorine, tungsten-molybdenum-chlorine, and tungsten-oxygen. The interesting possibility arose of a system with hot and cold surfaces of different materials, both of them simultaneously stable within some band of operating conditions.

INTRODUCTION

Successful operation of energy-converting or energy-producing devices for extended periods at elevated temperatures entails the solution of many difficult materials problems. One of these is the sublimation of hot surfaces. The possibility of minimizing or eliminating this effect by means of chemical reactions has been suggested. In such a process, a suitable gaseous material is introduced into a space between the hot surface and a cold surface. This gas reacts with the metal vapor

from the hot surface to form a gaseous compound. The compound returns the metal to the hot surface and deposits it.

This process was described by Langmuir (ref. 1) in connection with a tungsten filament sealed into a bulb containing a low chlorine pressure. Subsequent investigators have designed incandescent bulbs around this principle. Zubler and Mosby (ref. 2) constructed what is claimed to be the first practical lamps employing the regenerative cycle, using iodine vapor and argon.

Systems regenerated by chemical transport as in the cycle advocated for light bulbs involve stationary states of the first order. De Groot (ref. 3, pp. 24, 64, and 205) defines a stationary state of the first order as one in which all net flows of matter cease, but an energy flow exists. The steady-state regenerative system involving chemical transport has not yet been treated in detail.

On the other hand, Schäfer, et al. (refs. 4 to 6) studied chemical transport in which material in the solid state at one temperature is transported in the form of a gaseous compound through a temperature gradient and redeposited in a purified form at another temperature. The total system in such an application is not in a stationary state of the first order, since a solid phase at one temperature is growing at the expense of a solid phase at another temperature. By using diffusion equations to describe the mass transport of species, and by assuming local chemical equilibrium, Schäfer, et al. in reference 4 were able to express the rate of transport. A criterion for the direction of transport (cogradient or contragradient to the temperature) and efficiency of transport was developed in reference 5, based on the thermodynamics of the materials.

In contrast to the studies of Schäfer, et al., the present report deals with the stationary state of the first order. It is concerned with the thermodynamic requirements under which chemical transport may be expected to oppose the loss of metal from hot to cold surfaces by sublimation. Conditions under which the system including solids will remain stationary are described in simplified equations. Some systems of possible interest are investigated as examples in order to illustrate principles. These are the tungsten-chlorine (W-Cl) system, the molybdenum-chlorine (Mo-Cl) system, the tungsten-molybdenum-chlorine (W-Mo-Cl) system, and the tungsten-oxygen (W-O) system.

The present analysis, by describing the requirements for successful operation of diffusion-controlled systems, suggests a means of screening possible construction materials for testing in energy conversion devices. It is restricted to the assumptions of local chemical equilibrium, the applicability of gaseous diffusion equations to describe mass transport, and no convection. The processes are thus assumed to be diffusion-controlled. Quite possibly other steps in the process, such as surface

reactions, will govern under some conditions. Little is known about these reactions, especially at the very elevated temperatures considered herein.

No consideration was given to chemical interactions between species added to the interspace for their regenerative properties and materials that may be added for their effect on electrical properties. The particular materials considered in the examples herein were chosen because of the availability of thermal data, and are therefore not necessarily advocated for direct application in energy conversion devices.

ANALYSIS AND DISCUSSION

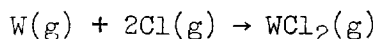
In this analysis, the principles are illustrated by considering the systems to contain few species. The simplified equations that result make evident the role of thermodynamic properties in the regenerative process.

The general approach followed in the analysis is to assume that conditions within the system are such that no net flow of matter is taking place. Equations describing this situation are then solved for limiting operating conditions and thermodynamic properties required to sustain a condition of no net flow of matter. It will be found in the simplified analysis that unless certain thermodynamic requirements are met, a regenerative process cannot prevent destruction of the solid surfaces.

The stoichiometric equation for chemical reactions may be written

$$-n_M M - n_X X = n_Y Y \quad (1)$$

(Symbols are defined in appendix A.) The use of negative signs for the stoichiometric coefficients on the left side of the stoichiometric equation permits the equilibrium equation to be written in an advantageous form. Regard M as the metal being transported, X as the gas introduced to react with it, and Y as the transporting compound. Thus, in the reaction



$$n_W = -1, \quad n_{Cl} = -2, \quad n_{WCl_2} = 1$$

By this convention the gas phase equilibrium between M , X , and Y is written

$$K_Y = (p_M)^{n_M} (p_X)^{n_X} (p_Y)^{n_Y} \quad (2)$$

At the outset, it is useful to discuss the directions in which the species involved in the reaction of equation (1) will be transported. As shown in appendix B (eq. (B10)) the mole flux of species i in chemical transport involving a single reaction is given by

$$\underline{W}_i = - \frac{n_i \lambda_r}{\Delta H_Y} \text{ grad } T \quad i = m, x, y \quad (3)$$

where ΔH_Y is the heat liberated by the reaction of equation (1) and λ_r , the thermal conductivity due to chemical reaction, is always positive. For metal atoms to be transported in product Y to a region of higher temperature, it is seen that ΔH_Y must be negative (exothermic reaction) inasmuch as n_Y is positive.

For purposes of discussion, several conditions of operation of the system will be considered. The simplest case will be treated first, with complexities being added subsequently. The cases considered are:

Case I. Condition for no loss of metal from the hot surface by condensation of its vapor on the cold surface

Case II. Condition for stability of hot and cold surfaces of different materials

Case III. Condition for no loss of hot surface by condensation of product

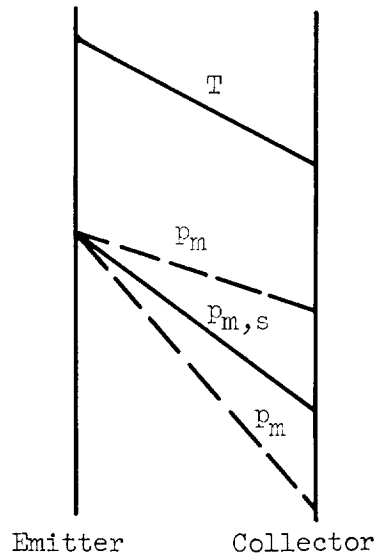
Case IV. Condition for a stable cold surface formed of metallic product containing no emitter metal

It is convenient herein to refer to the hot surface as the emitter and the cold surface as the collector. This is adopted from the nomenclature of thermionic devices, to which the regenerative cycles discussed herein might be applied.

Case I. Condition for No Loss of Emitter Metal by

Condensation of Vapor on Collector

Consider a situation in a system of emitter and collector as depicted in sketch (a):



(a)

Temperature profiles and partial pressure profiles will not in general be linear as shown.

To simplify the treatment of this case, the collector material will be assumed to be entirely inert, a restriction that will be removed in subsequent cases. The interspace between emitter and collector is assumed to behave as a continuum with chemical equilibrium throughout. Temperature and concentration jumps at the walls are assumed to be small. The vapor of the metal comprising the emitter is assumed to saturate the gas phase adjacent to the emitter surface; thus, since $(p_m)_e = (p_{m,s})_e$, all lines of p_m join at the emitter in the diagram. If the curve of p_m lies above the curve of $p_{m,s}$ throughout the interspace, condensation will occur in the interspace. The resulting particles of emitter metal will drift to the collector and accumulate. On the assumption that the curves of p_m and $p_{m,s}$ do not intersect in the interspace, a condition for no metal to condense in the interspace adjacent to the emitter is that the curve of p_m be steeper than the saturation curve:

$$\left[RT^2 \frac{d(\ln p_m)}{dT} \right]_e > \left[RT^2 \frac{d(\ln p_{m,s})}{dT} \right]_e$$

By the Clausius-Clapeyron equation,

$$RT^2 \frac{d(\ln p_{m,s})}{dT} = \Delta H_{v,m}$$

Thus the condition that the curve of p_m be steep enough to prevent condensation adjacent to the emitter is

$$\left[RT^2 \frac{d(\ln p_m)}{dT} \right]_e > \Delta H_{v,m} \quad (4)$$

The concentration gradients are now considered for the simplest case of the single gas phase reaction of equation (1) occurring in the interspace with chemical equilibrium. Since the concentration of M must decrease away from the emitter to prevent saturation of M in the interspace, the flux of M will be away from the emitter. Equation (3) shows that ΔH_y must be negative for the product Y to transport metal M back to the emitter.

If species M and Y are in much lower concentration than reactants X, the gradient of the logarithm of the metal partial pressure (herein-after called the metal pressure gradient parameter) is written

$$RT^2 \frac{d(\ln p_m)}{dT} = \frac{\Delta H_y/n_m}{1 + \frac{\Delta_{xy}}{\Delta_{xm}} \left(\frac{n_y}{n_m} \right)^2 \frac{p_m}{(K_y p_m^{-n_m} p_x^{-n_x})^{1/n_y}}} \quad (5)$$

(see appendix B). When this is substituted in inequality (4) and rearranged, setting

$$(p_m)_e = (p_{m,s})_e$$

the following criterion is obtained for no condensation in the interspace adjacent to the emitter:

$$\frac{\Delta H_y/n_m}{1 + \frac{\Delta_{xy}}{\Delta_{xm}} \left(\frac{n_y}{n_m} \right)^2 \frac{(p_{m,s})_e}{(K_y p_{m,s}^{-n_m} p_x^{-n_x})^{1/n_y}}} > \Delta H_{v,m} \quad (6)$$

Since n_m is negative and ΔH_v is always positive, this expression can be satisfied only if $\Delta H_y / (n_m \Delta H_{v,m}) > 1$. For $n_m = -1$, it is necessary that $-\Delta H_y > H_{v,m}$. If expression (6) is taken as an equality, it may be solved for the minimum partial pressure p_x of reactant X required for no condensation adjacent to the emitter. In particular, for the case where $-n_m = n_y$ and $\Delta_{xy} = \Delta_{xm}$

$$p_x = K_y^{1/n_x} \left(\frac{1}{\frac{-\Delta H_y}{n_m \Delta H_{v,m}} - 1} \right)^{-n_y/n_x} \quad (7)$$

There is a possibility that the slope of p_m , although steeper at the emitter than that of $p_{m,s}$, might lessen in the interspace resulting in intersection with $p_{m,s}$. Such intersection, at least for the simple cases satisfying the assumptions used in this section, will be shown to be unlikely.

If the equations of $\ln p_m$ and $\ln p_{m,s}$ are expanded in a Taylor series about the temperature of the emitter and the difference is taken, it is found that

$$\begin{aligned} \ln p_{m,s} - \ln p_m &= (\ln p_{m,s} - \ln p_m)_e + \left[\frac{d(\ln p_{m,s})}{dT} - \frac{d(\ln p_m)}{dT} \right]_e \Delta T + \\ &\quad \frac{1}{2!} \left[\frac{d^2(\ln p_{m,s})}{dT^2} - \frac{d^2(\ln p_m)}{dT^2} \right]_e (\Delta T)^2 + \dots \end{aligned}$$

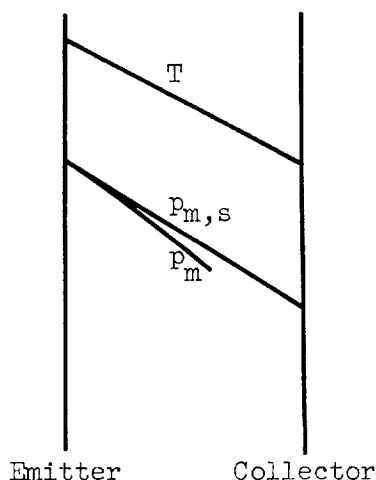
According to inequality (B19), a pressure of reactant X sufficient to make the curves of p_m and $p_{m,s}$ coincident at the emitter results in

$$\left[\frac{d^2(\ln p_{m,s})}{dT^2} \right]_e > \left[\frac{d^2(\ln p_m)}{dT^2} \right]_e$$

For coincidence at the emitter

$$(\ln p_{m,s})_e = (\ln p_m)_e \quad \text{and} \quad \left[\frac{d(\ln p_{m,s})}{dT} \right]_e = \left[\frac{d(\ln p_m)}{dT} \right]_e$$

From the difference in the Taylor expansions it may then be seen that $p_{m,s} \geq p_m$. As one proceeds toward lower temperatures, the curve of p_m therefore steepens with respect to that of $p_{m,s}$ and falls below, as shown in sketch (b).



(b)

Coincidence of the curves of $p_{m,s}$ and p_m across the interspace cannot occur, and intersection of the curves in the interspace seems unlikely. Moreover, if p_x exceeds the minimum required for coincidence of the curves at the emitter, so that the curves diverge even at the emitter, the improbability of intersection in the interspace should be even greater.

Case II. Condition for Stability of Emitter and Collector of Different Materials

In Case I, the collector was assumed for simplicity to be inert. This restriction will be removed in the present case so that the compatibility of the emitter and collector can be investigated.

It was shown in Case I that coincidence of the curves of $p_{m,s}$ and p_m could not occur across the interspace, and that their intersection was unlikely. From Case I it may be deduced that an emitter and collector of the same material very likely cannot be stable together in the same system. The possibility remains that, by making emitter and collector of different materials, both will remain unattacked over an appreciable range of p_x .

Initially consider that the emitter is inert. The condition that the collector metal not be deposited on the emitter is then that

$$p'_m < p'_{m,s}$$

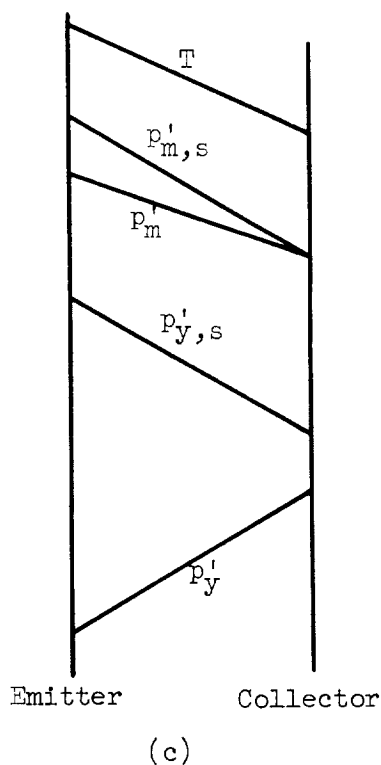
where the primes denote collector material. Assume that the interspace at the collector is saturated with collector metal. It is then necessary that

$$\left[\frac{d(\ln p'_m)}{dT} \right]_c < \left[\frac{d(\ln p'_{m,s})}{dT} \right]_c$$

or

$$\left[RT^2 \frac{d(\ln p'_m)}{dT} \right]_c < \Delta H'_{v,m} \quad (8)$$

The situation may be pictured thus:



The criterion for a stable collector is established from inequality (8) by steps similar to those in going from inequalities (4) to (6). The

resulting expression differs only in the direction of the inequality:

$$\frac{\frac{\Delta H'_Y/n'_m}{1 + \frac{\Delta'_{xy}}{\Delta'_{xm}} \left(\frac{n'_y}{n'_m}\right)^2} (p'_{m,s})_e}{\left[K'_Y(p'_{m,s})^{-n'_m} (p'_x)^{-n'_x}\right]_e^{1/n'_y}} < \Delta H'_{v,m} \quad (6a)$$

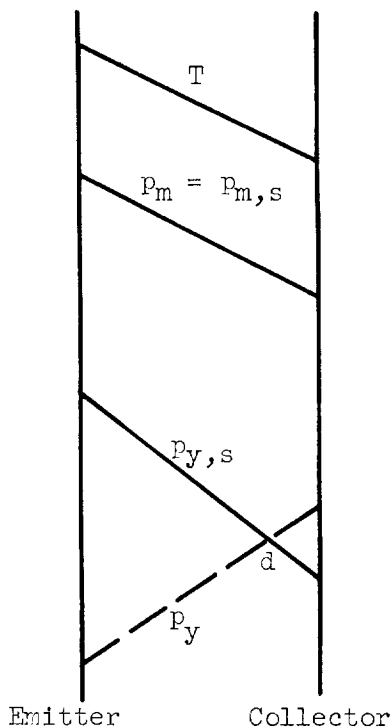
If $\Delta H'_Y$ is negative, the ratio $\Delta H'_Y/n'_m$ will be positive. Inequality (6a) can then be satisfied only up to some maximum value of p'_x . For $-n'_m = n'_y$ this maximum value may be found from equation (7). On the other hand, if $\Delta H'_Y$ is positive, the inequality can be satisfied for all p'_x .

Now consider a system in which neither emitter nor collector is inert. If they are to be compatible when $\Delta H'_Y$ is negative, the minimum p_x required for a stable emitter must be less than the maximum permitted for a stable collector. The zone between these pressures is the region available for stable operation.

Case III. Condition for No Loss of Emitter

by Condensation of Product

While the conditions dictated by inequality (6) may assure no direct loss of metal from the emitter by metallic condensation, a net loss of metal may occur by condensation of the product at the collector. Assume that a saturation pressure of the product above its condensed phase is described by a curve $p_{y,s}$. If the intercept d of $p_{y,s}$ and p_y occurs at a higher temperature than that desired for the collector face (see sketch (d)), product Y will condense on the collector until the point d is reached, or until the supply of emitter metal M or reactant X is depleted. This process constitutes a combustion of the emitter.



(d)

The permissible temperature difference between emitter and collector to prevent this condensation of product on the collector may be found as follows. The Clausius-Clapeyron equation for the saturation pressure of product Y may be integrated to relate the saturation pressure for Y at the emitter to that at point d:

$$(\ln p_{y,s})_d = (\ln p_{y,s})_e + \frac{\Delta H_{v,y}}{R} \frac{\Delta T}{T_e T_d} \quad (9)$$

where $\Delta T = T_d - T_e$. Assume that the partial pressure of Y is simply related to temperature by the following equation for the pressure gradient parameter of product:

$$RT^2 \frac{d(\ln p_y)}{dT} = C_y \quad (10)$$

where C_y is a constant. Integration relates the partial pressure of Y at the emitter to that at station d where $p_{y,s}$ equals p_y :

$$\ln(p_{y,s})_d = (\ln p_y)_e + \frac{C_y \Delta T}{RT_e T_d} \quad (11)$$

Combining equations (9) and (11) yields

$$\Delta T = \frac{\frac{RT_e^2 \ln(p_{y,s}/p_{y,e})}{C_y - \Delta H_{v,y}}}{1 - \frac{RT_e \ln(p_{y,s}/p_{y,e})}{C_y - \Delta H_{v,y}}} \quad (12)$$

The value of ΔT occurring at the minimum p_x required to prevent loss of the emitter by sublimation is of the greatest interest. The minimum p_x from inequality (6) and the saturation pressure of p_m at the emitter temperature are used in equation (2) to find $p_{y,e}$. For the case where species M and Y are in small concentration compared to X, C_y at the minimum p_x becomes:

$$C_y = \frac{\Delta H_y}{n_y} - \frac{n_m}{n_y} \Delta H_{v,m} \quad (13)$$

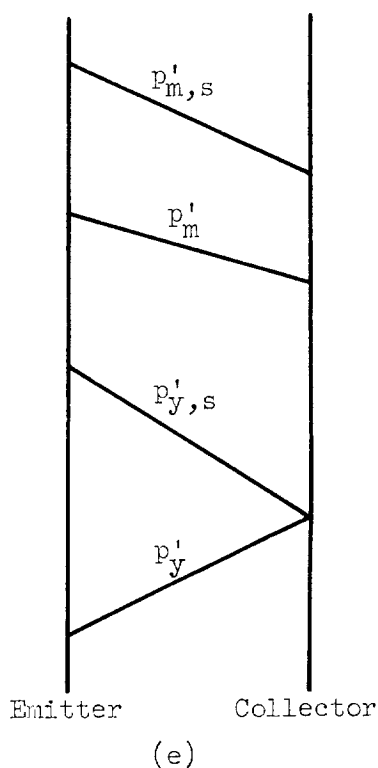
(see eq. (B14)).

As p_x is increased beyond the minimum required to satisfy inequality (6), p_y also increases. Under the conditions assumed for this simplified analysis, the absolute value of ΔT will be decreased. Indeed, sufficiently high p_x may cause product Y to condense on the emitter!

Case IV. Condition for a Stable Collector Formed of Metal Product Containing No Emitter Metal

For some reason or another, a collector formed of the product of some metal other than the emitter metal may be desirable or tolerable. If electric currents are present in the system, consideration will then have to be given to the electrical conductivity of this product.

The condition that product exist on the collector is that at the collector $p'_{y,s} = p'_y$. At the same time, the partial pressure of free metal M' must be less than the saturation pressure of M' at the collector. Otherwise free metal M' may condense at the collector in preference to its product Y'. The situation might be as pictured in sketch (e):

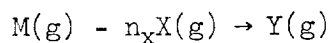


In this case of the nonmetallic collector, some minimum pressure of reactant X is needed to assure saturation of Y' at the collector temperature. While there is then no upper limit imposed upon the pressure of reactant X because of requirements of the collector, the emitter may be destroyed by condensation of its product on the collector as discussed in Case III.

Summary Remarks Concerning Cases I, II, III, and IV

A simple system has been considered in this analysis to make clear the role of thermal properties of materials in the regenerative process. The system consists of reactant gas X , emitter metal M , and collector metal M' , and their gaseous products Y and Y' . The concentration of X is assumed to be much higher than that of any other species.

In the simplest case the stoichiometric equation for the reaction among the gaseous species may be written as



Chemical transport will then counter the loss of emitter metal through condensation, provided

$$-\Delta H_Y > \Delta H_{V,m}$$

Even though the materials under consideration satisfy this requirement, the partial pressure p_X of the reactant gas must exceed some minimum value.

For a metallic collector to be stable in this system over a useful range of pressure, it must first of all be made of different material than the emitter. If $\Delta H_Y'$ for product Y' of a metallic collector is negative, a maximum p_X exists for which the collector will be stable. This p_X must exceed the minimum p_X for stability of the emitter if the collector and emitter are to be compatible.

Even though loss of emitter metal by sublimation is countered by introduction of the reactant gas X , the product Y may condense at the temperature chosen for the collector. The resulting net loss in emitter material can be avoided by raising the collector temperature.

If the vapor pressure p_Y' of the collector metal product is higher than the saturation pressure $p_{Y,s}'$, the collector will be formed of a metal product instead of metal. In some cases it may be necessary to avoid forming the collector of product, while in others a collector formed of product may be desirable.

The analysis suggests that an initial screening of materials for use in regenerative systems will require knowledge of the following thermal data at elevated temperatures: (1) The heat of formation of the transporting product Y or Y' from the gaseous emitter or collector metal and the reactant gas, (2) the heats of vaporization and vapor pressures of emitter and collector metals, and (3) heats of vaporization and vapor pressure of products Y and Y' .

For systems meeting the restrictions placed on the derivations, the minimum p_X of equation (7) and the ΔT of equation (12) are figures of merit. For systems of greater thermodynamic complexity these expressions may be unsuitable, but the insight they embody may be quite valuable. Furthermore, they may provide a means of screening quickly materials for systems that are to be regenerated by chemical transport.

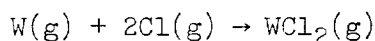
EXAMPLES

W-Cl System

The halogen-tungsten systems are known by experiment to be regenerative, as has been mentioned. Sufficient thermochemical data exist to permit the characteristics of operation in the region of gas continuum to be estimated by the principles in the ANALYSIS AND DISCUSSION section.

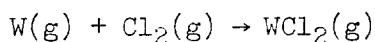
At low temperatures, the W-Cl system considered herein contains all tungsten chlorides up to WCl_6 . At the elevated temperatures of chief interest in thermionic devices, WCl_2 tends to be the predominant chloride. Brewer, et al. (ref. 7, pp. 276-311) suggest the possible importance of WCl but present no data on this species. Typical composition curves for the W-Cl system on page 284 of reference 7 show WCl_2 predominating above $2000^\circ K$ at pressures up to 1 atmosphere.

Thermal data from references 7 and 8 have been combined as discussed in appendix C to enable an assessment of the W-Cl system to be made. At $3000^\circ K$ the following data result:



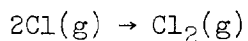
$$\Delta H_y = -246.1 \text{ kcal}$$

$$K_y = p_{WCl_2} / p_W p_{Cl}^2 = 6.31 \times 10^5$$



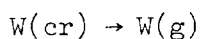
$$\Delta H_y = -184.6 \text{ kcal}$$

$$K_y = p_{WCl_2} / p_W p_{Cl_2} = 5.7 \times 10^7$$



$$\Delta H = -61.51 \text{ kcal}$$

$$K = 1.11 \times 10^{-2}$$



$$\Delta H_v = 202.63 \text{ kcal}$$

$$K = p_W = 1.3 \times 10^{-7} \text{ atm}$$

While there are four species considered to be present in the W-Cl system, namely, W, WCl₂, Cl, and Cl₂, it is possible in a simple analysis to ignore either Cl or Cl₂. This is accomplished by dealing only with two regions of pressure. One region is that in which Cl far exceeds Cl₂ so that the latter may be neglected, leaving only W, WCl₂, and Cl. The other region is that in which Cl₂ far exceeds Cl in importance, leaving W, WCl₂, and Cl₂. At 3000° K a Cl pressure of 1 atm results in a Cl₂ pressure of only 0.011 atm. In fact, these pressures do not become equal until the Cl pressure reaches 91.2 atm.

Consider first the low-pressure region where Cl predominates over Cl₂. Let the emitter temperature be 3000° K and assume that the diffusion coefficients are all equal. Use of the data for the reaction $W(g) + 2Cl(g) \rightarrow WCl_2(g)$ in inequality (6) shows that indeed a pressure p_{Cl_2} may be found that will satisfy the inequality:

$$\frac{246.1}{1 + \frac{1}{Kp_{Cl}^2}} > 202.63$$

so that the requirement for no condensation of tungsten is met. Moreover, the minimum pressure of Cl required is found by equation (7) to be 2.1 mm Hg, which justifies the neglect of Cl₂. Evaluation of equation (5) for the tungsten pressure gradient parameter at a monatomic chlorine pressure much higher than this low limit, but below the pressure of appreciable diatomic chlorine, shows that

$$\begin{aligned} RT^2 \frac{d(\ln p_W)}{dT} &= \frac{246.1}{1 + \frac{1}{Kp_{Cl}^2}} \\ &= 246.1 \text{ kcal for } Kp_{Cl}^2 \gg 1 \end{aligned}$$

This value of 246.1 kcal for the tungsten pressure gradient parameter represents an upper bound in the region where only monatomic chlorine is important.

On the other hand, if the chlorine pressure is raised until diatomic chlorine predominates, substitution in inequality (6) would require for no condensation that

$$\frac{184.6}{1 + \frac{1}{K_{pCl_2}}} \geq 202.63$$

This inequality cannot be satisfied by any real pressure, so that condensation must occur in the interspace at pressures where diatomic chlorine is important. Evaluation of equation (5) in this region shows that

$$\begin{aligned} RT^2 \frac{d(\ln P_W)}{dT} &= \frac{184.6}{1 + \frac{1}{K_{pCl_2}}} \\ &= 184.6 \text{ kcal for } K_{pCl_2} \gg 1 \end{aligned}$$

To examine the region where Cl and Cl₂ are of similar concentration, a more general expression for tungsten pressure gradient parameter, admitting the coexistence of four species, W, Cl, Cl₂, and WCl₂, was evaluated. The expression is derived in appendix B as equation (B9). For want of precise numbers all diffusion coefficients were again set equal to each other. The range of total pressure P was from 10⁻⁴ to 10⁺⁶ mm Hg, and emitter temperatures ranged from 2000° to 3000° K. The pressure range chosen incorporated those regions already discussed where either monatomic or diatomic chlorine may be ignored. The upper pressures exceed both the limit of practical interest and the limit of validity of the ideal gas law. Nevertheless, the adverse effect of diatomic reactant on metal pressure gradient parameter illustrated at these higher pressures may occur in other systems within pressure ranges of interest.

The data for the entire range of pressures are plotted in figure 1 in terms of tungsten pressure gradient parameter against P_{mm} for several emitter temperatures. The curve for any temperature is seen to rise from a very low value to about 246 kcal as total pressure is increased. This represents the effect of increasing monatomic chlorine pressure in a region where diatomic chlorine is unimportant. As total pressure is increased, the tungsten pressure gradient parameter approaches a value of 185 kcal because of the growing predominance of diatomic chlorine. These bounds were indicated by the calculations made previously using the simplified equations. The heat of vaporization of tungsten is represented as a line at 202.6 kcal. For the system to be chemically regenerated, that is, for no condensation to occur in the interspace, this line must be exceeded. At 3000° K the minimum total pressure is seen from figure 1 to be about 2 mm Hg. This is in agreement with the simplified calculation made previously, since the partial pressure of monatomic chlorine approximately equals the total pressure of the system at this condition.

A cross plot of figure 1 is shown as figure 2. The operable region of emitter temperature and total pressure for no condensation of tungsten in the interspace is bounded by two lines, outside of which condensation occurs in the interspace.

While no attack of the emitter may occur because of condensation of metal vapor in the interspace, the possibility of attack by condensation of product exists. The minimum temperature at which the collector may be operated without accumulating product was computed for the emitter operating at 3000°K with the minimum chlorine pressure of 2.1 mm Hg. The condensing species of product was assumed to be WCl_2 . Thermal data discussed in appendix C were used. The saturation pressure of tungsten at 3000°K and the minimum chlorine pressure of 2.1 mm Hg or 2.72×10^{-3} atm found previously gave $\ln p_{\text{WCl}_2}$ equal to -14.32. The estimated value of $\ln p_{\text{WCl}_2,s}$ was 3.658, and the heat of vaporization of WCl_2 at 3000°K was taken as 23 kcal. The resulting ΔT was -1850°K . A minimum collector temperature of 1150°K can thus be employed with an emitter temperature of 3000°K and a continuum in the interspace.

In reality, the condensing tungsten chloride might well be a species other than WCl_2 . At the lower temperatures other species predominate both in the gaseous and condensed phases (see ref. 7). However, the rather large ΔT of -1850°K is conservative, inasmuch as the estimated vapor pressure data in reference 7 indicate WCl_2 to be less volatile than the other tungsten chlorides at low temperatures.

If for any reason a chlorine pressure greater than the minimum needed to prevent metal condensation in the interspace is used, the absolute value of ΔT will lessen accordingly. This is because of the increase in WCl_2 pressure with chlorine pressure.

Mo-Cl System

The Mo-Cl system is thermodynamically similar to the W-Cl system (see ref. 7). Assuming the predominance of MoCl_2 at temperatures above 2000°K , a series of curves similar to those of figure 1 were calculated for the Mo-Cl system. The species considered were Mo, Cl, Cl_2 , and MoCl_2 . Reference 7 suggests the possible importance of MoCl , but for want of ready data this was not included, as in the case of WCl . The calculations were limited to an upper temperature of 2800°K by the melting point of molybdenum, 2870°K .

Figure 3 presents curves of molybdenum pressure gradient parameter plotted against P_{mm} for several emitter temperatures. Each curve rises to a value of about 203 kcal, corresponding to a fairly large value of p_{Cl} in the absence of appreciable diatomic chlorine. As the total pressure is increased, the tungsten pressure gradient parameter approaches a value of 143 kcal, because of the growing importance of diatomic chlorine. The heat of vaporization of molybdenum, in the neighborhood of 152.5 kcal, is shown in figure 3. Only on portions of the curves above the heat of vaporization will condensation not occur in the interspace.

Figure 4 is a cross plot of figure 3, showing the operable region for the Mo-Cl system in terms of emitter temperatures and total pressures. Both figures 3 and 4 resemble the corresponding ones for the W-Cl system.

Compatibility of a System with W as Emitter

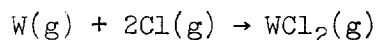
and Mo as Collector, Containing Cl

The possibility of a regenerative system containing chlorine, with a stable tungsten emitter and stable molybdenum collector, can be investigated by means of figures 1 and 3. For instance, suppose the emitter is at 3000° K. According to figure 1, a total pressure exceeding about 2 mm Hg is required for the tungsten pressure gradient parameter to exceed $(\Delta H_V)_W$. This is the condition for a stable emitter. From figure 3 it may be seen that at this total pressure molybdenum will satisfy inequality (8) for a stable collector at any temperature above 2600° K.

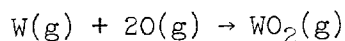
The range between stable emitter and collector temperatures is small in this example and might well be either erased or widened by uncertainties in thermal data or some nonideality of the real physical process. However, the possibility of building regenerative systems of dissimilar metals or alloys and suitable reactants may merit experimental effort.

W-O System

Experimental evidence as to the use of O in a regenerative system is claimed by Dushman (ref. 8, p. 680). It is mentioned that barium chlorate was found to regenerate light bulb filaments under some conditions. A theoretical computation of the W-O system makes an interesting comparison with the W-Cl and Mo-Cl system. The force binding O to W is stronger than that binding Cl to W. For instance, at 3000° K for the reaction



a ΔH_y of -246 kcal is estimated. For the reaction



at 3000° K, a ΔH_y of -307 kcal is estimated (see appendix C). It is therefore not surprising that the equilibriums among species in the W-O system follow a quite different pattern from those in the W-Cl system. This in turn affects what is to be expected of the operation of the W-O system.

The principal thermodynamic characteristic of the W-O system, as discussed in appendix C, is its great complexity at elevated temperatures. Because of the large number of species involved and the low mole fractions of monatomic and diatomic oxygen in the system, simplified calculations cannot be made. As a result, the general equations of appendix B must be used.

With the assumption that all diffusion coefficients are equal, equation (B9) was evaluated for the W-O system at temperatures of 2600°, 2800°, and 3000° K over pressures ranging roughly from 10^{-3} to 10^3 mm Hg. Eight species were considered: W, WO, WO₂, WO₃, W₃O₉, W₄O₁₂, O, and O₂. The assumption of equal diffusion coefficients is undoubtedly quite poor in view of the complex molecules such as W₃O₉ present.

Figure 5 shows the variation of tungsten pressure gradient coefficient with P_{mm} at emitter temperatures of 2600°, 2800°, and 3000° K. The limiting value of pressure gradient parameter, below which condensation of tungsten will occur in the interspace adjacent to the emitter, is shown as a line at 202.6 kcal, the heat of vaporization of tungsten. Because of the complexity of the W-O system, it is not possible to relate the features of the curves in figure 5 to the appearance or disappearance of the various species, such as was done for the W-Cl system. Figure 6 is a cross plot of figure 5, showing the operable region within which no condensation of tungsten will occur in the interspace adjacent to the emitter.

Comparison of figures 2 and 6 shows that the lower pressure limit of operation for the W-O system is smaller by nearly two orders of magnitude than for the W-Cl system. The upper limit is also smaller, but converges toward the lower limit with increasing temperature in the W-O system, instead of remaining relatively parallel to the lower limit as in the W-Cl system. At 3000° K the resulting operable region is relatively narrow.

Figure 6 shows the operable region where no condensation occurs adjacent to the emitter. There is no assurance that it will not occur elsewhere in the interspace. In contrast to the W-Cl system, the product

species appear in concentrations approaching or exceeding the concentrations of the reactants O and O₂. The arguments made in ANALYSIS AND DISCUSSION concerning the improbability of intersection of the $p_{m,s}$ and p_m lines throughout the interspace apply only to cases where the reactant is by far the most abundant species. In the case of the W-O system, only direct integration of the gradient equations across the interspace will determine for sure whether condensation can occur.

For this same reason, the calculation of a ΔT between emitter and collector, such that no condensation of oxide will occur on the collector, becomes uncertain. However, it is quite interesting to make a computation of ΔT for the W-O system, with some assumptions.

Assume that C_y of equation (10) is constant across the interspace for WO₃ and its polymers and that each of these in turn is the only condensing species. Equation (12) will then apply individually to each oxide and may be solved for a ΔT . Such a computation was made for species WO₃, W₃O₉, and W₄O₁₂ at 3000° K using C_y , the pressure gradient parameter for these species, as given by figure 7. Compositions indicated by figure 8 (appendix C) were used.

The following brief table shows the results at several pressures starting with 0.056 mm Hg, the minimum operable pressure for the W-O system at 3000° K, according to figure 5:

Species assumed to be condensing	System pressure, P, mm Hg			
	0.056	0.1	1.0	10
	Temperature difference between collector and emitter, °K			
WO ₃	-584	-554	-394	-662
W ₃ O ₉	-584	-554	-394	-661
W ₄ O ₁₂	-583	-554	-394	-661

The principal factors in making the absolute value of T in the W-O system so much smaller than in the W-Cl system are the larger absolute values of C_y . At 3000° K and the minimum operable pressure, $C_y - \Delta H_{v,y}$ is -342 kcal for WO₃ and only -66.5 kcal for WCl₂. While $\Delta H_{v,y}$ plays a role, the dominant effect is due to the C_y . Because

$p_{y,s}$ and p_y enter equation (12) logarithmically, they play a subordinate role in determining ΔT .

The analysis indicates that a hot tungsten surface will be chemically regenerated by oxygen under the proper conditions. This is in accord with the interpretation given by Dushman (ref. 8) to the mechanism by which barium chlorate regenerates light-bulb filaments. Dushman does not credit the chlorine with any role in the regenerative process, but part of the mechanism may well be due to the chlorine.

CONCLUDING REMARKS

In the foregoing analysis, an attempt was made to draw guide lines for examining regenerative cycles involving materials of interest in high-temperature devices. The analysis, while restricted to gas continuum conditions, should introduce method into the selection of candidate materials for use in the regenerative systems.

The analysis was based upon considerations of thermodynamic properties of materials and upon mass transport phenomena in gas continua. The influence of thermal properties was illustrated by considering some hypothetical systems. Other systems may be examined in similar fashion. An interesting possibility arose as a result of these calculations, namely, the construction of devices with both stable emitters and collectors. From the analysis and the examples it may be concluded that a preliminary screening of materials for use in regenerative systems will require the following information at elevated temperatures: (1) Heats of formation of the gaseous products responsible for chemical transport from the gaseous emitter or collector metal and the reactant gas, (2) the heats of vaporization and vapor pressures of the metals and their products, and (3) gaseous species present in the systems of interest.

No consideration was given to the possibility that other parts of the system might be destroyed by the very reactants used to regenerate the emitter and collector. Also, the effect of regenerative reactants upon other materials in the working fluid, such as the cesium used in thermionic devices, was not considered.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, December 5, 1961

APPENDIX A

SYMBOLS

A	coefficient used to determine mole flux vector \underline{W} of dependent species when only one distinct reaction is present
A_{ij}	an element of the matrixes used to compute mole flux vector \underline{W}_i of dependent species.
C_y	pressure gradient parameter of product at conditions where the parameter is assumed to be constant
$ D $	denominator determinant in expression for mole flux vector \underline{W}_i
D_{ik}	binary diffusion coefficient
F_T^O	free energy per mole, including chemical energy, at temperature T and standard conditions
ΔF	free-energy change
grad	gradient
H_T^O	enthalpy per mole, including chemical energy, at temperature T and standard conditions
$ \Delta H _i$	numerator determinant in expression for mole flux vector \underline{W}_i
ΔH_v	heat of evaporation or sublimation
ΔH	heat evolved in a reaction
K	equilibrium constant for a reaction
M	denotes metallic species in stoichiometric equation
n	with subscripts, denotes stoichiometric coefficients
P	total pressure, the sum of partial pressures
p	partial pressure of constituent of gas mixture
R	gas constant, 1.98718 cal/(mole)(°K)
T	temperature, °K
\underline{W}_i	mole flux vector of i^{th} component of a gas mixture

X	in stoichiometric eq. (1), denotes the substance added to react with the metal; with superscript, represents any species in a stoichiometric equation
x	mole fraction
Y	in a stoichiometric equation, denotes the metallic compound responsible for chemical transport
Δ	with subscripts, as Δ_{mx} or Δ_{lk} , a term related to the binary diffusion coefficient $\Delta_{lk} = RT/D_{lk}P$
λ_r	thermal conductivity due to chemical reaction

Subscripts:

c	collector
d	point of intercept of partial pressure curve p_y , for product Y with saturation curve $p_{y,s}$
e	emitter
i,j	i th or j th distinct chemical reaction in a mixture, or i th dependent species
k,l,n	species present in gas mixture
m	metal
mm	pressure, mm Hg
s	saturated
T	temperature, °K
v	vaporization
x	reactant with metal
y	pertains to compound of metal and gaseous reactant formed by the reaction, $-n_m M - n_x X = n_y Y$
v	total number of dependent reactions or species in gas mixture
μ	total number of species

APPENDIX B

GENERAL EQUATIONS OF CONCENTRATION GRADIENT

The problem of thermal conduction in mixtures of reacting gases at chemical equilibrium has been considered recently in references 9 and 10. Using concepts and equations contained therein, one can solve for the variation of concentration gradient with temperature gradient instead of for the thermal conductivity in the following manner. Suppose there are a total of μ species present, designated by subscripts k, l, n ($k, l, n = 1$ to μ). Of these species, the first v ($v < \mu$) may be regarded as the dependent species, separately designated where necessary by the subscripts i, j . Given the equilibrium constants for the v reactions forming the dependent species from the $\mu - v$ independent species, the partial pressures of the dependent species may be computed from the partial pressures of the independent species. The stoichiometric equations for the v reactions may be written in the manner of equation (1) as

$$\sum_{k=1}^{\mu} n_{ik} X^k = 0 \quad i = 1 \text{ to } v \quad (B1)$$

where the matrix of coefficients n_{ik} has the form

$$[n_{ik}] = \left[\begin{array}{ccccc|ccccc} n_{11} & 0 & 0 & \dots & 0 & n_{1,v+1} & \dots & n_{1\mu} \\ 0 & n_{22} & 0 & \dots & 0 & n_{2,v+1} & \dots & n_{2\mu} \\ 0 & 0 & n_{33} & \dots & 0 & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ 0 & 0 & 0 & 0 & n_{vv} & n_{v,v+1} & \dots & n_{v\mu} \end{array} \right]$$

Coefficients to the left of the partition are positive; those to the right are negative. At steady state with no sources or sinks the net flux of any one of the species k alone or combined in other molecules must satisfy the equation

$$\bar{W}_k = \sum_{i=1}^v \frac{\bar{W}_i}{n_{ii}} n_{ik} \quad k = 1 \text{ to } \mu \quad (B2)$$

Equation (B2) for the fluxes of the first ν species yields an identity. The equilibrium equations are written

$$K_i = \prod_{k=1}^{\mu} (p_k)^{n_{ik}} \quad i = 1 \text{ to } \nu$$

These may be differentiated to give

$$\frac{\Delta H_i}{RT^2} \text{grad } T = \sum_{k=1}^{\mu} \frac{n_{ik}}{x_k} \text{grad } x_k \quad i = 1 \text{ to } \nu \quad (\text{B3})$$

where $x_k = p_k/P$. However, according to Hirschfelder, et al. (ref. 11, p. 517), the diffusion equations in the absence of external force fields, total-pressure gradients, or thermal diffusion may be written

$$\text{grad } x_k = \sum_{l=1}^{\mu} \Delta_{lk} (x_l \underline{W}_k - x_k \underline{W}_l) \quad (\text{B4})$$

Combining equations (B2), (B3), and (B4) gives

$$\frac{-\Delta H_j}{RT^2} \text{grad } T = \sum_{i=1}^{\nu} \frac{W_i}{n_{ii}} A_{ij} \quad (\text{B5})$$

where

$$A_{ij} = \sum_{k=1}^{\mu-1} \sum_{l=k+1}^{\mu} x_k x_l \Delta_{lk} \left(\frac{n_{ik}}{x_k} - \frac{n_{il}}{x_l} \right) \left(\frac{n_{jk}}{x_k} - \frac{n_{jl}}{x_l} \right) \quad (\text{B6})$$

The v equations represented by (B5) may be solved simultaneously for the fluxes of the dependent components:

$$\frac{W_i}{n_{ii}} = \frac{\begin{vmatrix} A_{11} & \dots & A_{1,i-1} & -\Delta H_1 & A_{1,i+1} & \dots & A_{1v} \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \\ A_{v1} & \dots & A_{v,i-1} & -\Delta H_v & A_{v,i+1} & \dots & A_{vv} \end{vmatrix}}{\begin{vmatrix} A_{11} & \dots & A_{1v} \\ \dots & \dots & \dots \\ A_{v1} & \dots & A_{vv} \end{vmatrix}} \frac{\text{grad } T}{RT^2} \quad (\text{B7})$$

where the values of ΔH are substituted in the i^{th} column of the determinant. Designate the numerator determinant so formed by $|\Delta H|_i$ and the denominator determinant by $|D|$. The concentration gradient of the l^{th} species is found by combining (B2), (B4), and (B7):

$$\text{grad } x_l = \sum_{i=1}^v |\Delta H|_i \sum_{k=1}^{\mu} \Delta_{lk} (n_{ik} x_l - n_{il} x_k) \frac{\text{grad } T}{|D| RT^2} \quad (\text{B8})$$

By rearrangement, the partial pressure gradient parameter found useful in this report results:

$$RT^2 \frac{d(\ln p_l)}{dT} = \frac{1}{x_l} \sum_{i=1}^v |\Delta H_i| \sum_{k=1}^{\mu} \frac{\Delta_{lk} (n_{ik} x_l - n_{il} x_k)}{|D|} \quad (\text{B9})$$

If a single reaction is occurring in the mixture, only one dependent species exists and equations (B2) and (B5) may be combined to get

$$- \frac{\Delta H}{ART^2} \text{grad } T = \frac{W_k}{n_k}$$

or

$$- \frac{\lambda_r}{\Delta H} \text{grad } T = \frac{W_k}{n_k} \quad (\text{B10})$$

where

$$\lambda_r = \frac{1}{A} \frac{\Delta H^2}{RT^2}$$

According to reference 9, λ_r , the thermal conductivity due to chemical reaction, is positive; therefore, $-\lambda_r/\Delta H$ will be positive only if ΔH is negative.

For the case of the single reaction, equation (B9) becomes

$$RT^2 \frac{d(\ln p_l)}{dT} = \frac{-\Delta H_y}{x_l A} \sum_{k=1}^{\mu} \Delta_{lk} (n_k x_l - n_l x_k)$$

since the determinants reduce to

$$|\Delta H| = -\Delta H_y$$

$$|D| = A$$

and where

$$A = \sum_{k=1}^{\mu-1} \sum_{n=k+1}^{\mu} x_k x_n \Delta_{kn} \left(\frac{n_k}{x_k} - \frac{n_n}{x_n} \right)^2$$

Therefore,

$$RT^2 \frac{d(\ln p_l)}{dT} = \frac{\Delta H_y}{x_l} \frac{\sum_{k=1}^{\mu} \Delta_{lk} (n_l x_k - n_k x_l)}{\sum_{k=1}^{\mu-1} \sum_{n=k+1}^{\mu} x_n x_k \Delta_{kn} \left(\frac{n_k}{x_k} - \frac{n_n}{x_n} \right)^2} \quad (B11)$$

If this is applied to the reaction of equation (1), and the partial pressures of species M and Y are less than the partial pressure of reactant X by an order of magnitude,

$$RT^2 \frac{d(\ln p_m)}{dT} = \frac{\Delta H_y / n_m}{1 + \frac{\Delta_{xy} \left(\frac{n_y}{n_m} \right)^2 \frac{p_m}{p_y}}$$

$$RT^2 \frac{d(\ln p_y)}{dT} = \frac{\Delta H_y / n_y}{1 + \frac{\Delta_{xm} \left(\frac{n_m}{n_y} \right)^2 \frac{p_y}{p_m}}$$

Substituting the chemical equilibrium (eq. (2)) gives

$$RT^2 \frac{d(\ln p_m)}{dT} = \frac{\Delta H_y / n_m}{1 + \frac{\Delta_{xy} \left(\frac{n_y}{n_m} \right)^2 \frac{p_m}{\left(K_y p_m^{-n_m} p_x^{-n_x} \right)^{1/n_y}}} \quad (B12)$$

$$RT^2 \frac{d(\ln p_y)}{dT} = \frac{\Delta H_y / n_y}{1 + \frac{\Delta_{xm} \left(\frac{n_m}{n_y} \right)^2 \frac{\left(K_y p_m^{-n_m} p_x^{-n_x} \right)^{1/n_y}}{p_m}} \quad (B13)$$

For the case of the minimum pressure of reactant X satisfying inequality (6), equation (B13) for the interspace adjacent to the emitter becomes

$$RT^2 \frac{d(\ln p_y)}{dT} = \frac{\Delta H_y}{n_y} - \frac{n_m}{n_y} \Delta H_{v,m} \quad (B14)$$

The second derivative of the curve of $\ln p_m$ will now be compared with that of $\ln p_{m,s}$ in the simple case for which equation (B12) is valid, namely, that $p_x \gg p_y, p_m$. Assume ΔH_y to be constant with temperature. Also let $-n_m = n_y = 1$. It may be found from equation (B12), after some manipulation, that

$$\frac{d^2}{dT^2} (\ln p_m) = -\frac{2}{T} \frac{d}{dT} (\ln p_m) + \frac{\Delta H_y}{RT^2} \frac{d}{dT} (\ln p_m) + \left[\frac{d}{dT} (\ln p_m) \right]^2 \quad (B15)$$

Suppose that p_x is just sufficient to make the curves of p_m and $p_{m,s}$ coincident at the emitter. Then, by the Clausius-Clapeyron equation

$$\left[\frac{d(\ln p_m)}{dT} \right]_e = \left[\frac{d(\ln p_{m,s})}{dT} \right]_e = \left(\frac{\Delta H_{v,m}}{RT^2} \right)_e$$

Substituting this in equation (B15) yields

$$\frac{d^2}{dT^2} (\ln p_m)_e = \left[\left(\frac{\Delta H_{v,m}}{RT^2} \right)^2 - \frac{2}{T} \frac{\Delta H_{v,m}}{RT^2} + \left(\frac{\Delta H_y}{RT^2} \right) \left(\frac{\Delta H_{v,m}}{RT^2} \right) \right]_e \quad (B16)$$

From the Clausius-Clapeyron equation, the second derivative of $\ln p_{m,s}$ may be written

$$\frac{d^2}{dT^2} (\ln p_{m,s}) = - \frac{2}{T} \left(\frac{\Delta H_{v,m}}{RT^2} \right) \quad (B17)$$

where $\Delta H_{v,m}$ is also assumed constant with temperature. Combining equations (B16) and (B17) gives

$$\frac{d^2}{dT^2} (\ln p_m)_e = \frac{d^2}{dT^2} (\ln p_{m,s})_e + \left(\frac{\Delta H_{v,m}}{RT^2} \right)_e \left(\frac{\Delta H_{v,m}}{RT^2} + \frac{\Delta H_y}{RT^2} \right)_e \quad (B18)$$

In Case I of ANALYSIS AND DISCUSSION it was found that, for these curves to be coincident at any pressure, it was necessary for $\Delta H_y / (n_m \Delta H_{v,m}) > 1$. Since it has been assumed that $n_m = -1$, $\Delta H_{v,m} < -\Delta H_y$ in equation (B18). Because ΔH_y is negative, the entire second term on the right of equation (B18) is negative. The second derivative of $\ln p_m$ at the emitter is then less than that of $\ln p_{m,s}$ or

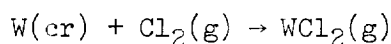
$$\left[\frac{d^2}{dT^2} (\ln p_m) \right]_e < \left[\frac{d^2}{dT^2} (\ln p_{m,s}) \right]_e \quad (B19)$$

APPENDIX C

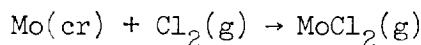
THERMAL DATA

W-Cl and Mo-Cl Systems

The heats of vaporization and vapor pressure of molybdenum and tungsten were taken from reference 12. The heats and free energies of formation of the gaseous dichlorides from the solid metals and diatomic chlorine at various temperatures were taken from reference 7. The heats of formation were

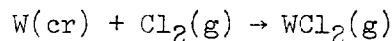


$$\Delta H_y = 18 \text{ kcal}$$



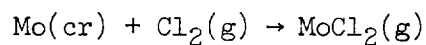
$$\Delta H_y = 10 \text{ kcal}$$

The corresponding free energies of formation were linearly extrapolated from 2000° K. These were, for WCl_2 ,



$$\Delta F_y = -2000 - 10(T - 2000) \text{ kcal}$$

and for MoCl_2 ,



$$\Delta F_y = -9000 - 9(T - 2000) \text{ kcal}$$

From these values, the heats and free energies of formation of the bi-chlorides from the gaseous metals and from either monatomic or diatomic chlorine were computed at desired temperatures thus:

$$(\Delta H)_{\text{M(g)} + \text{Cl}_2(\text{g}) \rightarrow \text{MCl}_2(\text{g})} = (\Delta H)_{\text{M(cr)} + \text{Cl}_2(\text{g}) \rightarrow \text{MCl}_2(\text{g})} - (\Delta H)_{\text{M(cr)} \rightarrow \text{M(g)}}$$

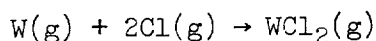
$$(\Delta F)_{\text{M(g)} + \text{Cl}_2(\text{g}) \rightarrow \text{MCl}_2(\text{g})} = (\Delta F)_{\text{M(cr)} + \text{Cl}_2(\text{g}) \rightarrow \text{MCl}_2(\text{g})} - (\Delta F)_{\text{M(cr)} \rightarrow \text{M(g)}}$$

and

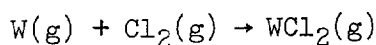
$$(\Delta H)_{M(g)+2Cl(g) \rightarrow MCl_2(g)} = (\Delta H)_{M(g)+Cl_2(g) \rightarrow MCl_2(g)} - (\Delta H)_{Cl_2(g) \rightarrow 2Cl(g)}$$

$$(\Delta F)_{M(g)+2Cl(g) \rightarrow MCl_2(g)} = (\Delta F)_{M(g)+Cl_2(g) \rightarrow MCl_2(g)} - (\Delta F)_{Cl_2(g) \rightarrow 2Cl(g)}$$

The heat and free energy of dissociation of chlorine were from unpublished NASA tables. At 3000° K the heats of formation from gaseous elements were for tungsten dichloride:

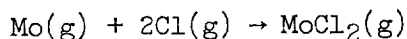


$$\Delta H_y = -246.1 \text{ kcal}$$

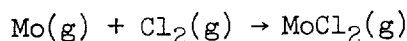


$$\Delta H_y = -184.6 \text{ kcal}$$

At 2400° K the heats of formation were for molybdenum dichloride:

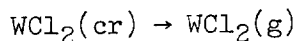


$$\Delta H_y = -142.5 \text{ kcal}$$



$$\Delta H_y = -203.5 \text{ kcal}$$

The pressure of WCl_2 vapor above its own solid was taken from an estimation on page 310 of reference 7:



$$\Delta F_v = 53,000 + 10T(\ln T) - 105T$$

Data for the tungsten chlorides contained in reference 7 are very tentative. They may eventually be found to be in conflict even at relatively low temperatures with experimental data that have been subsequently determined (see ref. 13).

W-O System

Thermal data for species in the W-O system were obtained as follows:

The heats and free energies of formation, ΔH_T^O and ΔF_T^O , of gaseous WO , WO_2 , and WO_3 from gaseous atoms at temperatures T were computed from the relations

$$(\Delta H_T^O)_{\text{atoms}} = (\Delta H_O^O)_{\text{atoms}} + (H_T^O - H_O^O)_{WO_n(g)} - (H_T^O - H_O^O)_{W(g)} - n(H_T^O - H_O^O)_{O(g)}$$

where

$$(\Delta H_T^O)_{\text{atoms}} = (H_T^O)_{WO_n(g)} - (H_T^O)_{W(g)} - n(H_T^O)_{O(g)}$$

$$(\Delta F_T^O)_{\text{atoms}} = (\Delta F_O^O)_{\text{atoms}} + (F_T^O - H_O^O)_{WO_n(g)} - (F_T^O - H_O^O)_{W(g)} - n(F_T^O - H_O^O)_{O(g)}$$

where

$$(\Delta F_T^O)_{\text{atoms}} = (F_T^O)_{WO_n(g)} - (F_T^O)_{W(g)} - n(F_T^O)_{O(g)}$$

Values of ΔH_O^O and ΔF_O^O were taken from De Maria, et al. (ref. 14); $(H_T^O - H_O^O)$ and $(F_T^O - H_O^O)$ were computed from information in the same source; and $(H_T^O - H_O^O)$ and $(F_T^O - H_O^O)$ for $W(g)$ were taken from reference 12, while for atomic oxygen they were taken from unpublished NASA tables.

The vapor pressure of WO_3 above its own condensed phase was computed from the free-energy change across the vaporization:



$$(\Delta F_T^O)_v = -RT \ln(p_s)_{WO_3}$$

where

$$\begin{aligned} (F_T^O)_{WO_3(g)} = & (\Delta F_T^O)_{\text{atoms}} + \frac{3}{2}(F_T^O - H_O^O)_{O_2(g)} + (F_T^O - H_O^O)_{W(\text{cr})} \\ & + \frac{3}{2} \left[(F_T^O)_{O(g)} - \frac{(F_T^O)_{O_2(g)}}{2} \right] + (F_T^O)_{W(g)} - (F_T^O)_{W(\text{Cr})} \end{aligned}$$

The data for O_2 were also from unpublished NASA tables. Enthalpies of elements in their standard states were assigned to be zero at $0^\circ K$.

Physical and thermodynamic properties of $WO_3(cr)$ were taken from Kubaschewski and Evans (ref. 15). The free energy and enthalpy of $WO_3(cr)$ were obtained by integration using empirical specific heat equations therein. The entropy of melting of $WO_3(cr)$ was taken to be the same as that listed for $MoO_3(cr)$, while the specific heat of $WO_3(l)$ was taken the same as the specific heat of $WO_3(cr)$ at the melting point. From these data the enthalpy and free energy of $WO_3(l)$ were computed up to $3000^\circ K$.

The W-O system is complicated by the existence of polymers of $WO_3(g)$ that far exceed $WO_3(g)$ in importance at some conditions. Berkowitz, et al. (ref. 16) found that the principal species above $WO_3(cr)$ in the neighborhood of $1400^\circ K$ were $W_3O_9(g)$ and $W_4O_{12}(g)$ in a mass spectro-metric analysis, with virtually no $WO_3(g)$ appearing. From their listed heats and entropies of sublimation and vapor pressures, the free energies and enthalpies of $W_3O_9(g)$ and $W_4O_{12}(g)$ up to $3000^\circ K$ were calculated using estimated specific heats and the previously discussed data for $WO_3(g)$. The specific heat of $W_3O_9(g)$ was estimated to be roughly 60 cal/(mole)($^\circ K$), between 1368° and $3000^\circ K$, or about three times that of $WO_3(g)$. The specific heat of $W_4O_{12}(g)$ similarly was estimated to be 80 cal/(mole)($^\circ K$). Heats of formation ΔH_f of the oxides of tungsten from gaseous tungsten and monatomic oxygen resulting from the computations are as follows at $3000^\circ K$:

$WO(g)$	-164 kcal
$WO_2(g)$	-307 kcal
$WO_3(g)$	-456 kcal
$W_3O_9(g)$	-1620 kcal
$W_4O_{12}(g)$	-2183 kcal

Figure 8 illustrates the composition of the W-O system at $3000^\circ K$ when the thermal data described above are used. The mole fractions of $W(g)$, $WO(g)$, $WO_2(g)$, $WO_3(g)$, $W_3O_9(g)$, $W_4O_{12}(g)$, $O(g)$, and $O_2(g)$ are shown as a function of total pressure in mm Hg. Figure 9 shows the variation of composition of the W-O system with temperature at a total pressure of 0.03 mm. In calculating the data of figures 8 and 9, the partial pressure of W was assumed to be the saturation pressure of W above crystal W.

The most notable feature is the sharp rise in concentration of the polymers of WO_3 with pressure and sharp decrease with temperature. This seems consistent both with the findings of Berkowitz, et al. (ref. 16) and Drowart, et al. (ref. 17). The former, as previously mentioned, found at temperatures of about 1400°K and pressures of about 10^{-2} mm Hg that the only species above $\text{WO}_3(\text{cr})$ were $\text{W}_3\text{O}_9(\text{g})$ and $\text{W}_4\text{O}_{12}(\text{g})$. The latter found $\text{WO}_3(\text{g})$ but none of its polymers in a Knudsen crucible containing Al_2O_3 at temperatures up to 2600°K .

The thermal data illustrated by figures 8 and 9 are of necessity quite rough. It is believed that the calculations of concentration gradient based upon them will illustrate trends. The assumption in the calculation of concentration gradients that all diffusion coefficients are the same may introduce errors of equal magnitude to those of thermal data.

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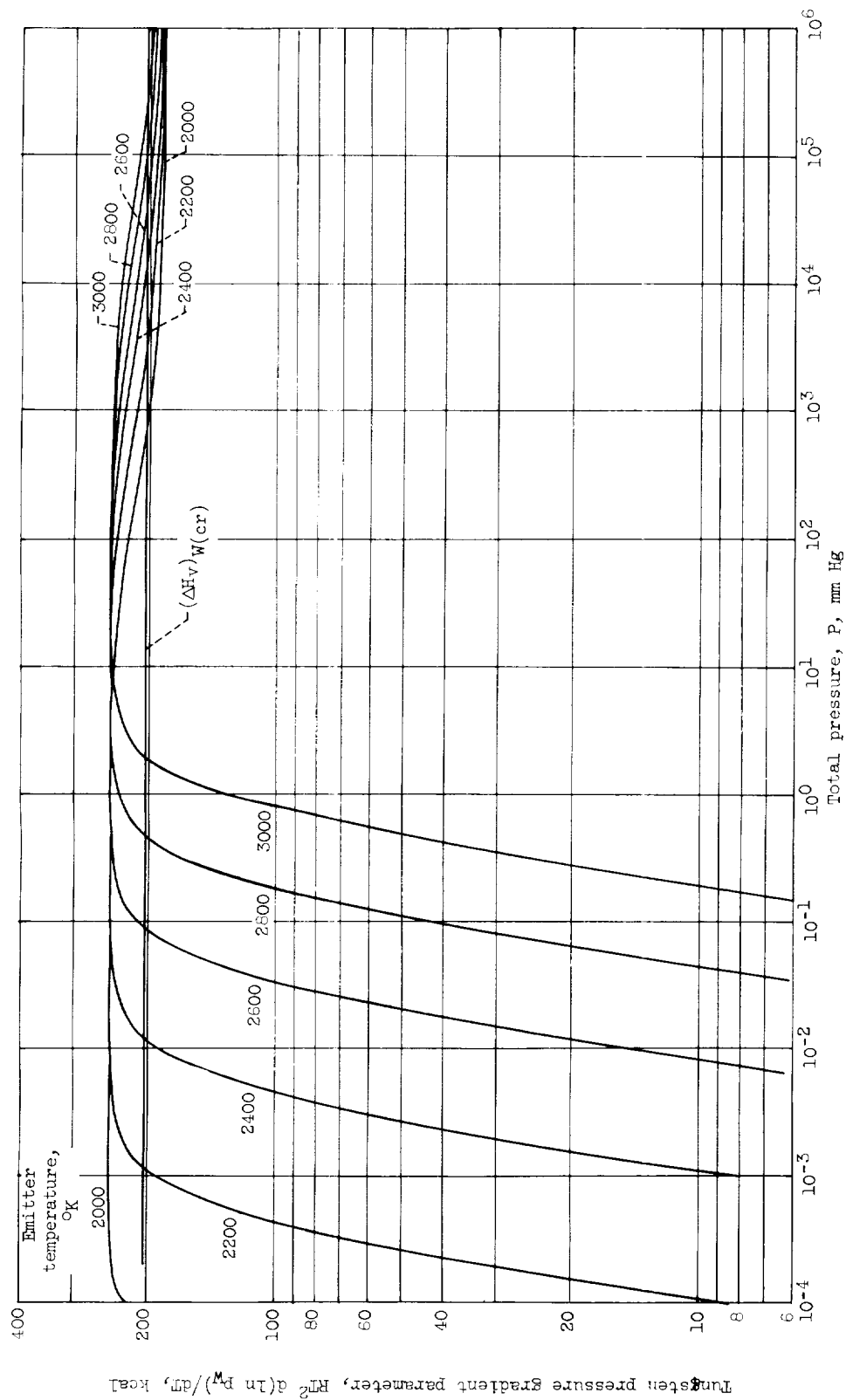


Figure 1. - Variation of tungsten pressure gradient parameter with total pressure at several emitter temperatures in W-Cl system.

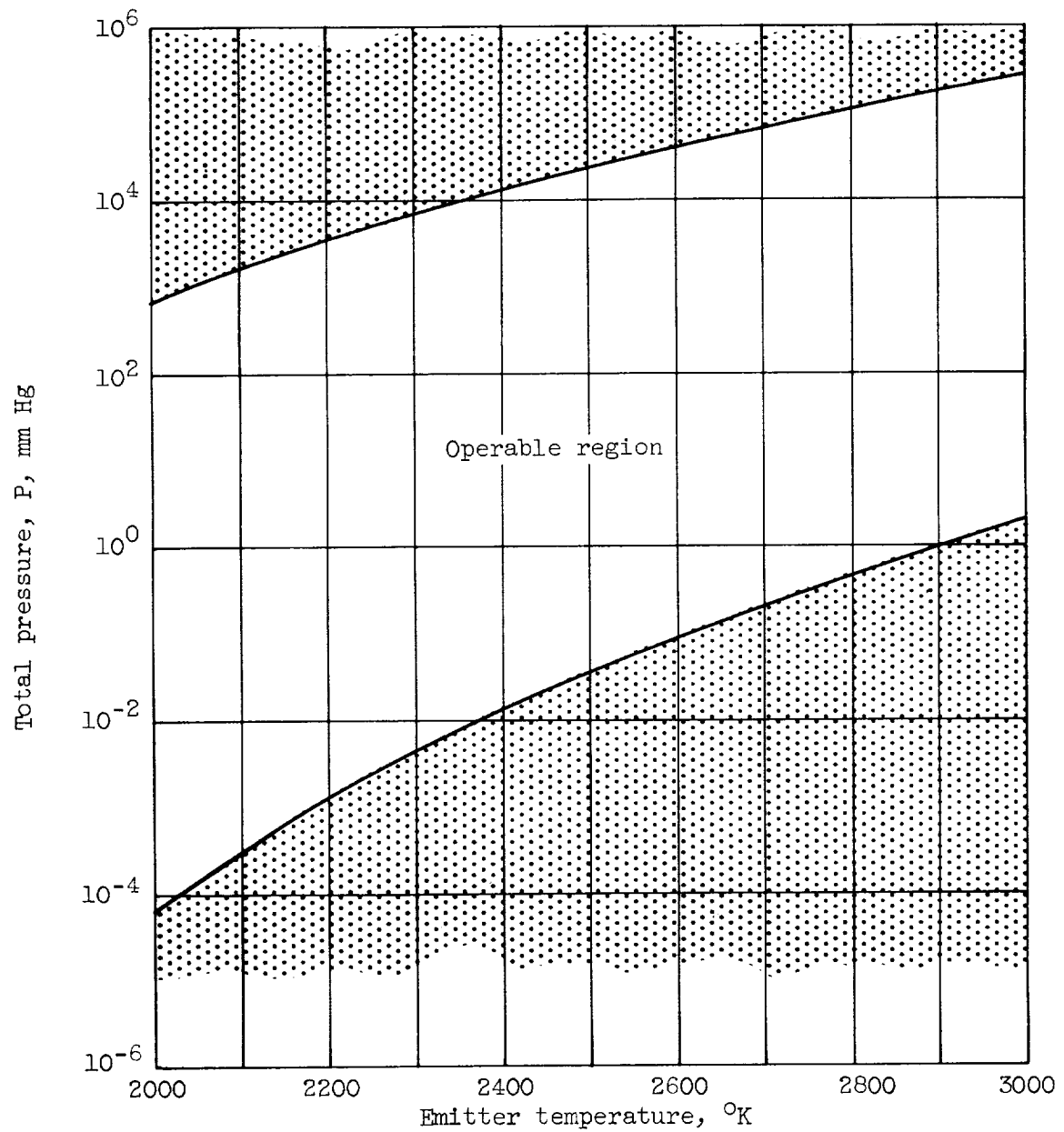


Figure 2. - Operable region of emitter temperature and total pressure for no condensation of tungsten in interspace for W-Cl system.

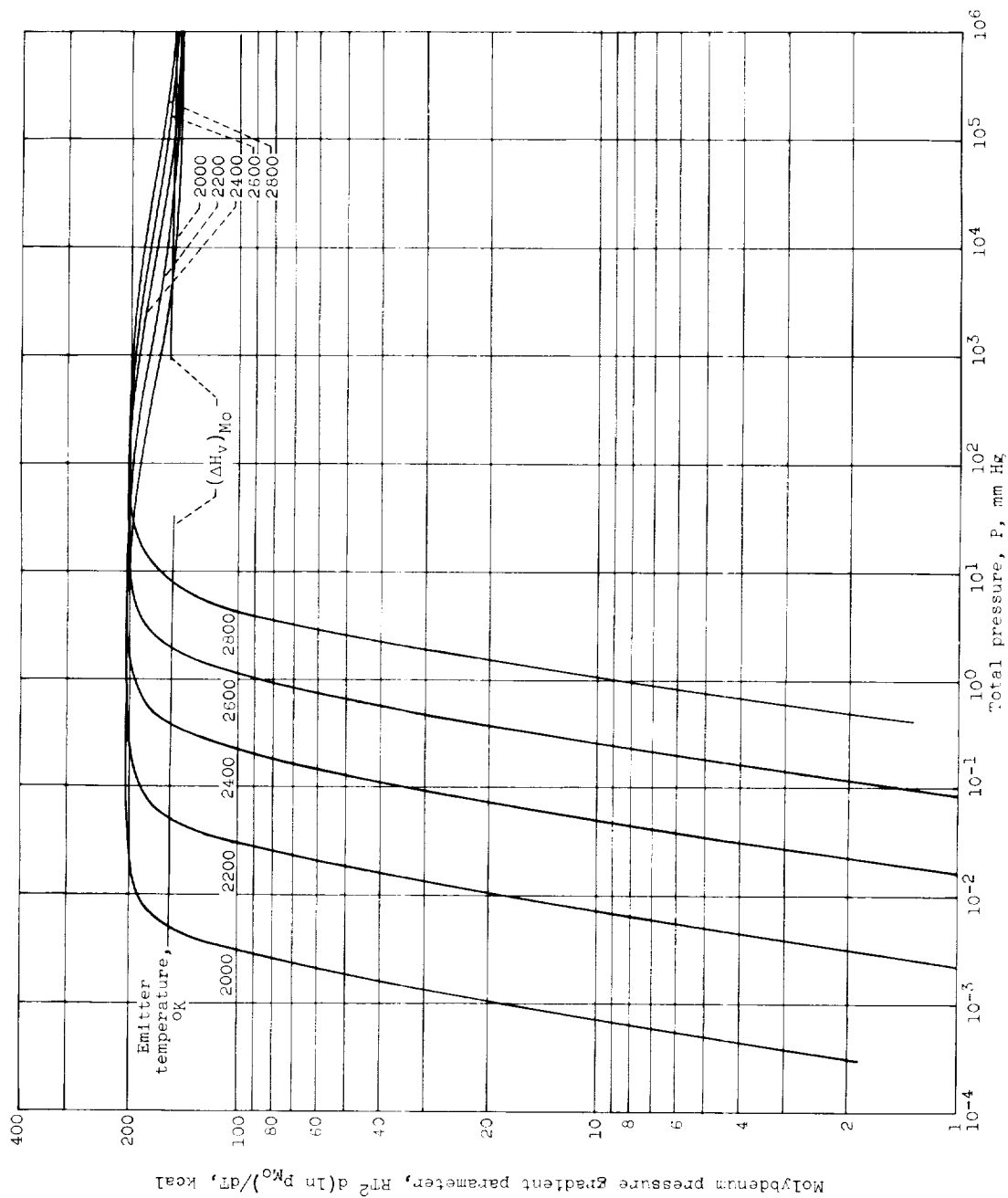


Figure 3. - Variation of molybdenum pressure gradient parameter with total pressure at several emitter temperatures in Mo-Cl system.

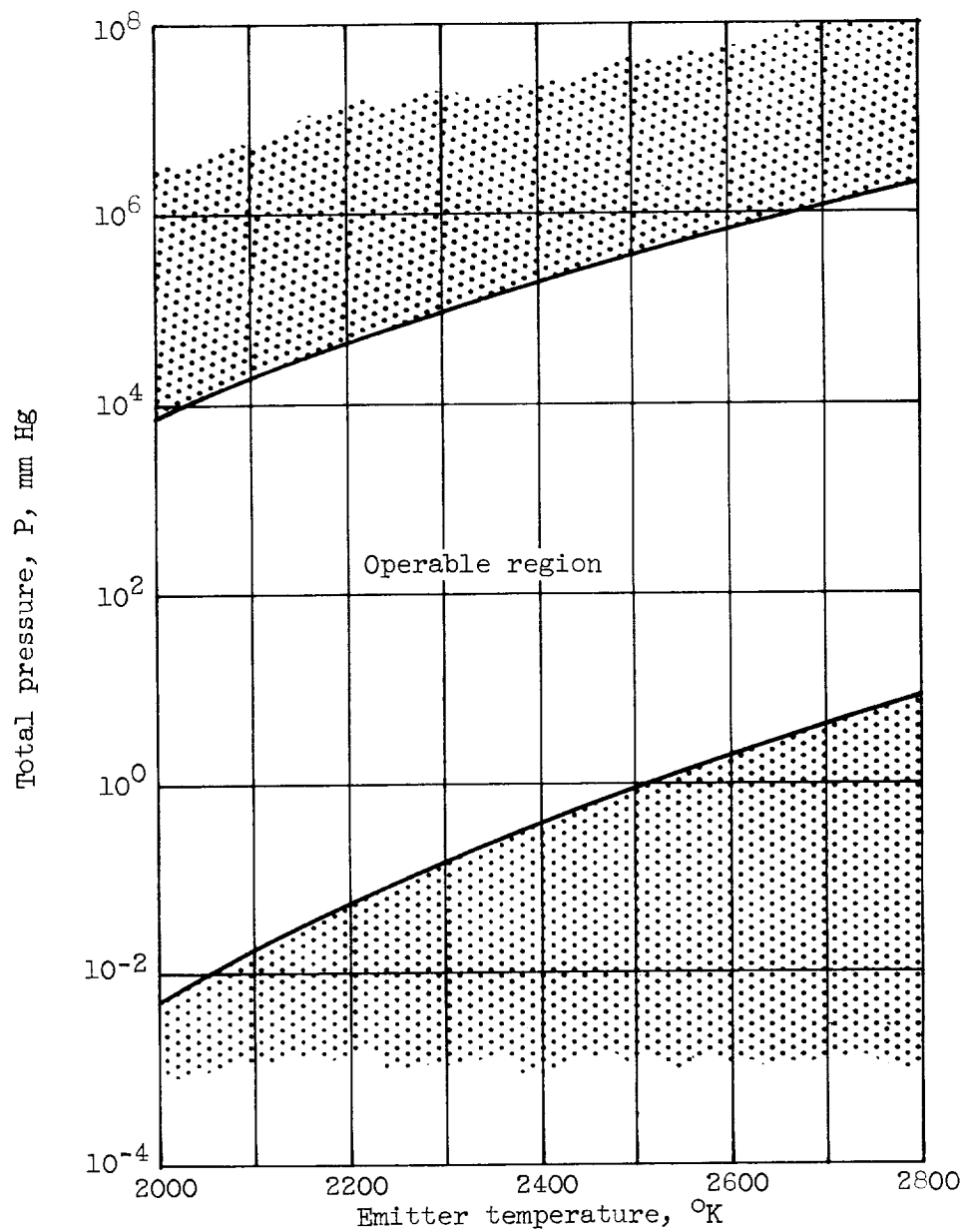


Figure 4. - Operable region of emitter temperature and total pressure for no condensation of molybdenum in the interspace for Mo-Cl system.

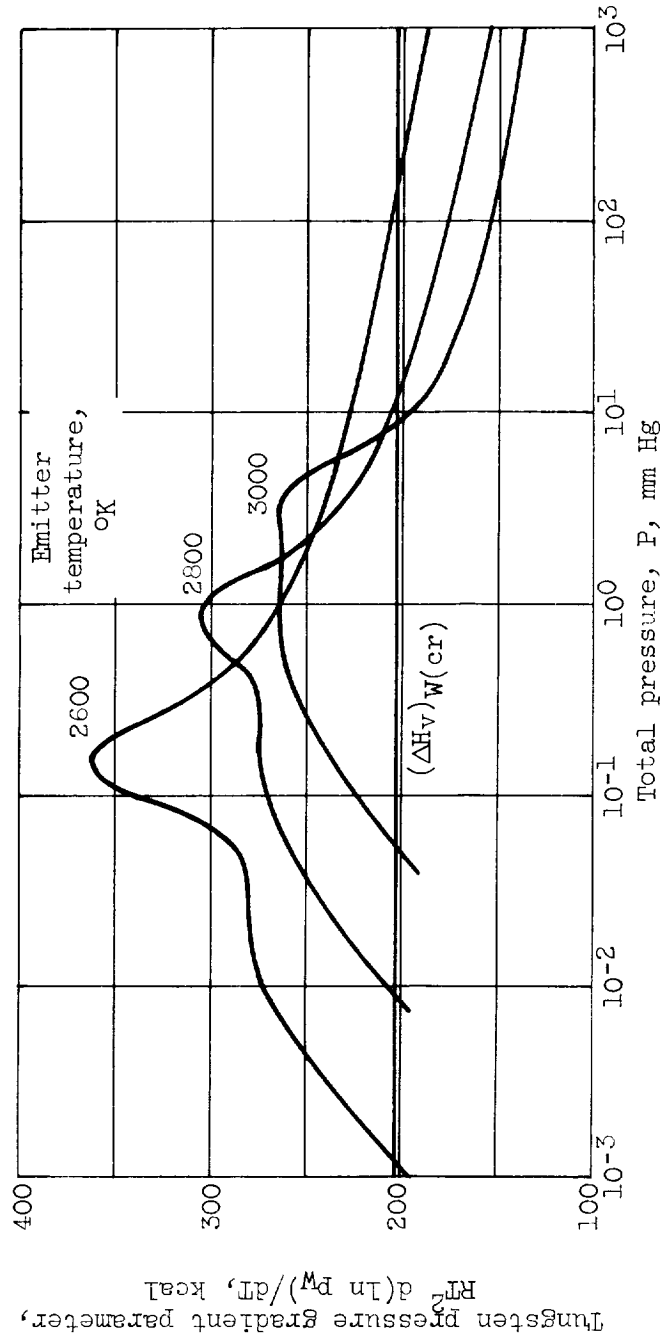


Figure 5. - Variation of tungsten pressure gradient parameter with total pressure at several emitter temperatures in W-O system.

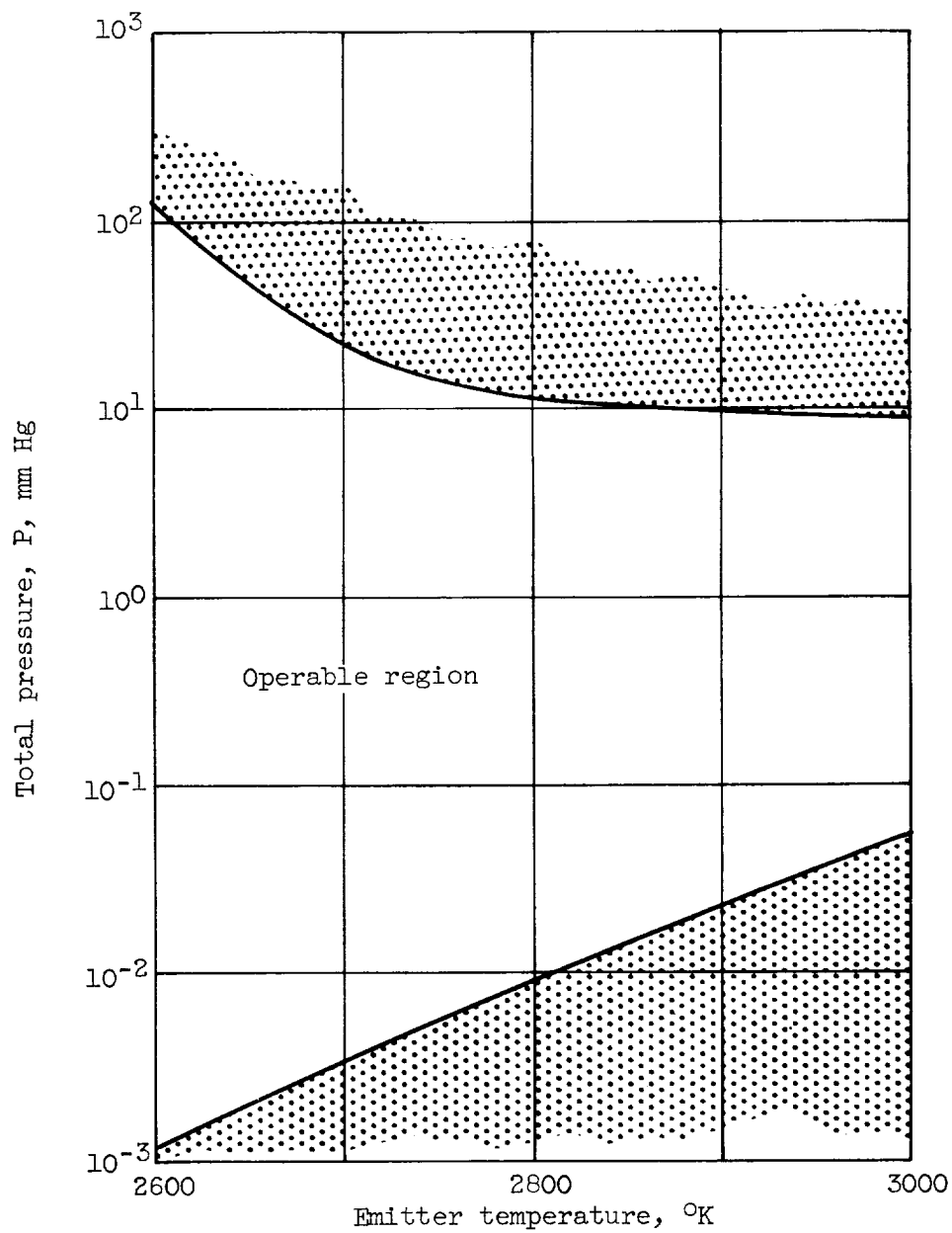


Figure 6. - Operable region of emitter temperature and total pressure for no condensation of tungsten in the interspace for W-O system.

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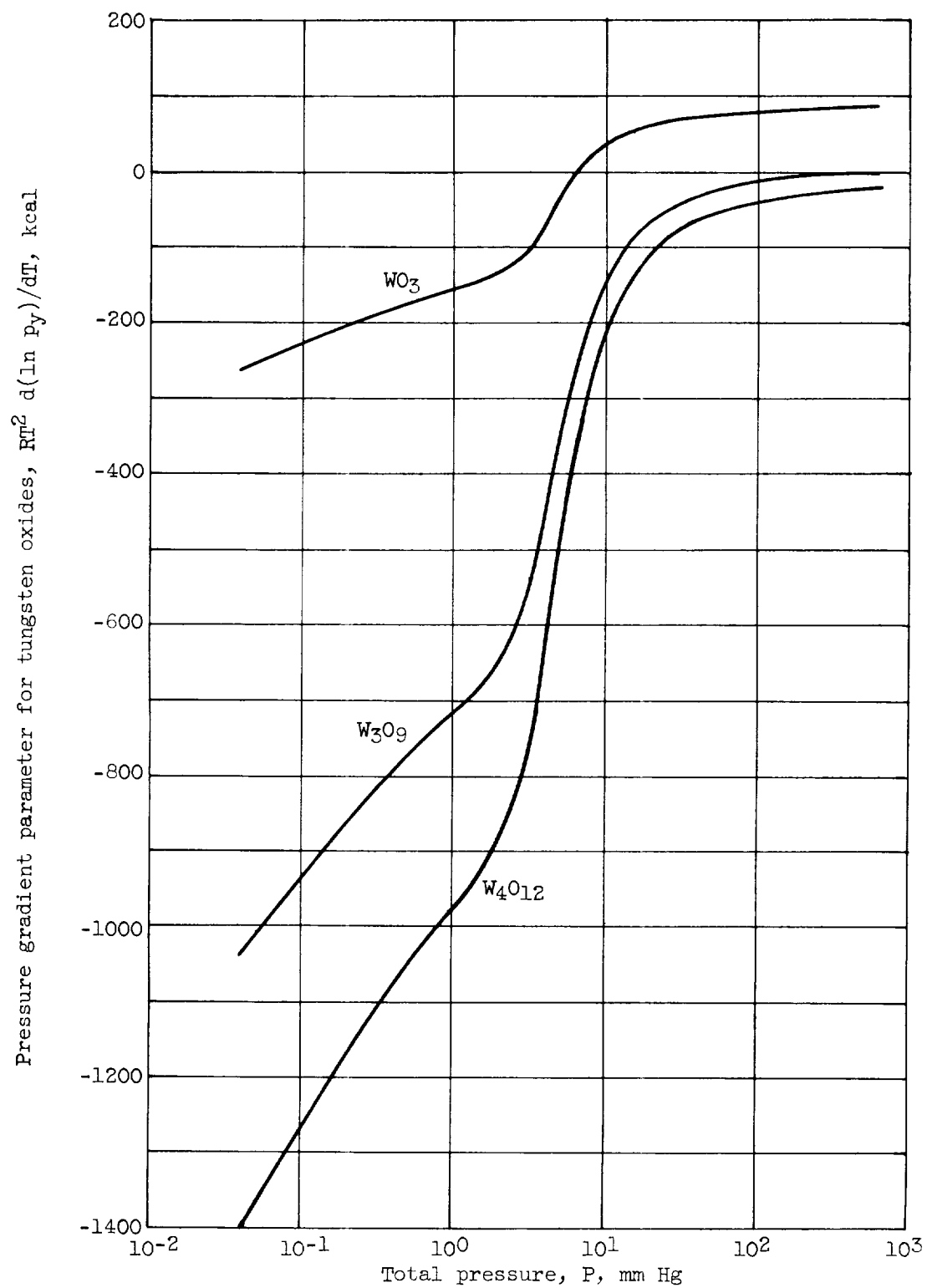


Figure 7. - Variation of pressure gradient parameter with total pressure at 3000° K for WO_3 , W_3O_9 , and W_4O_{12} .

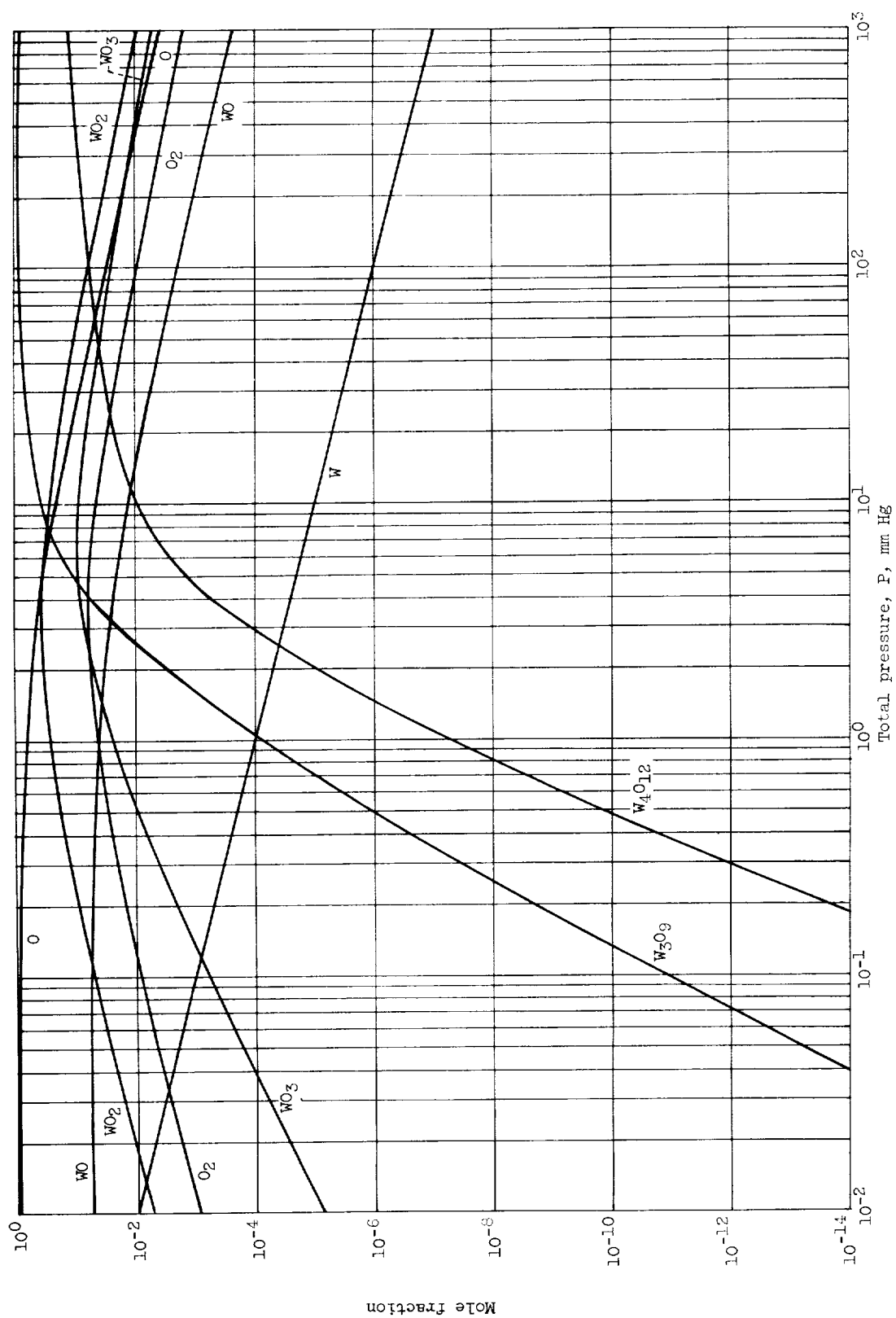


Figure 8. - Mole fractional composition in W-O system as a function of total pressure at 3000°K.

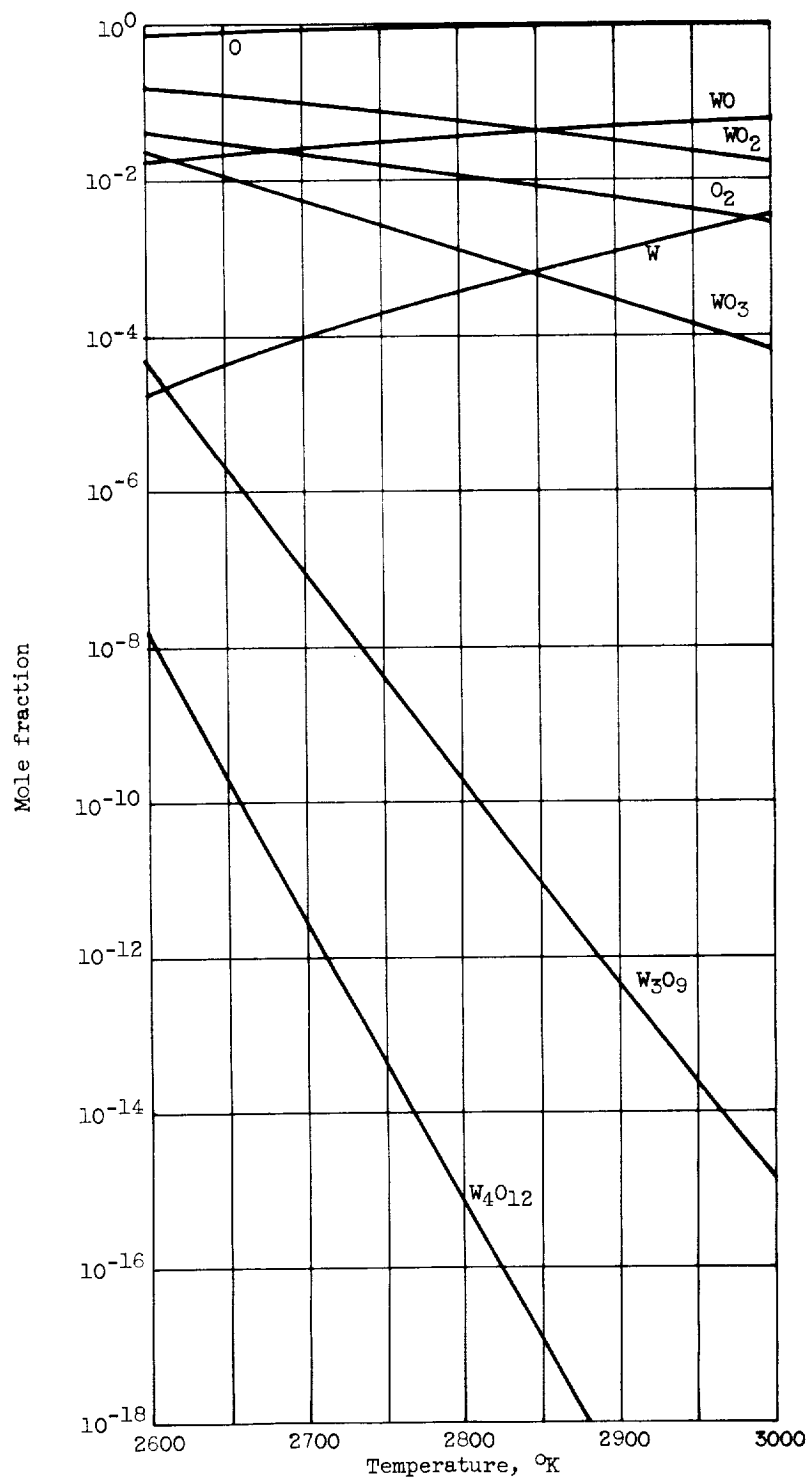


Figure 9. - Mole fractional composition in W-O system as a function of temperature at a total pressure of 0.03 mm.